

**This Page Is Inserted by IFW Operations
and is not a part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- **BLACK BORDERS**
- **TEXT CUT OFF AT TOP, BOTTOM OR SIDES**
- **FADED TEXT**
- **ILLEGIBLE TEXT**
- **SKEWED/SLANTED IMAGES**
- **COLORED PHOTOS**
- **BLACK OR VERY BLACK AND WHITE DARK PHOTOS**
- **GRAY SCALE DOCUMENTS**

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**

Japanese Kokai Patent Application No. Hei 7[1995]-137433



Job No.: 600-81611

Ref.: ELIZABETH GALLO KBH

Translated from Japanese by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. HEI 7[1995]-137433

Int. Cl. ⁶ :	B 41 M 5/00
Sequence Nos. for Office Use:	8808-2H
Filing No.:	Hei 5[1993]-286357
Filing Date:	November 16, 1993
Publication Date:	May 30, 1995
No. of Claims:	1 (Total of 9 pages; OL)
Examination Request:	Not filed

INKJET RECORDING SPECIALTY PAPER

Inventors:	Satoshi Maeda Central Research Laboratory Toyobo Co., Ltd. 2-1-1 Katada, Otsu, Shiga
	Yasunari Hotta Central Research Laboratory Toyobo Co., Ltd. 2-1-1 Katada, Otsu, Shiga
	Shigeru Yoneda Central Research Laboratory Toyobo Co., Ltd. 2-1-1 Katada, Otsu, Shiga
	Masanori Kobayashi Central Research Laboratory Toyobo Co., Ltd. 2-1-1 Katada, Otsu, Shiga
	Yozo Yamada Central Research Laboratory

Toyobo Co., Ltd.
2-1-1 Katada, Otsu, Shiga

Applicants:

000003160
Toyobo Co., Ltd.
2-2-8 Dojimahama
Kitaku, Osaka
Osaka

[There are no amendments to this patent.]

Abstract

Objective

Improvement of inkjet recording paper

Constitution

A cationic group-containing unsaturated polyester is dispersed in water and allowed to gradually coagulate to form particles which are then made into hollow crosslinked polyester having interior voids by void formation by thermal dewatering and crosslinking by seed polymerization, then an ink absorption layer comprising the particles and a binder on support paper surface [is formed].

Claim

Inkjet recording specialty paper, characterized by having a support covered by an ink absorption layer, wherein the absorption layer contains polyester-based hollow porous resin particles that contain 20-2000 Eq/ton cationic groups as the ionic group.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns inkjet recording specialty paper.

[0002]

Prior art

The inkjet recording process for forming characters or images by blowing fine ink droplets on recording paper has a low noise level and enables the equipment to be made small, thus it is widely used in industrial marking and OA printers. The inks for inkjet printing may be

oil-based or water-based, while for OA mainly water-based inks are used for environmental reasons. The most serious disadvantage of the inkjet recording process is that upon drying, the ink may clog the printhead, and to prevent this, humectants such as glycols, glycerin, etc., are compounded into the waterborne inks. However, the humectants introduced for the purpose of enhancing the reliability of the printhead may cause problems such as retardation of ink drying on the recording paper.

[0003]

To improve such problems concerning the recording paper, an ink absorption layer is formed on the recording paper surface for rapid absorption and drying of liquid components in the ink and also suppression of feathering to obtain enhanced recording quality. In general, inkjet recording paper can be classified as regular type or specialty paper. The regular type is not plain paper. It is rather a specialty paper size-pressed with retention of a plain paper-like touch. For the regular type, ink absorption is controlled by the type and amount of the body pigments and internal sizes used, surface treatment solution in the size press, etc. The body pigment may be talc, kaolin, calcined kaolin, silica, calcium carbonate, etc. The internal sizes may be rosin size, alkylketene dimer, etc., while starch, polyvinyl alcohol, etc., are used in the size press. When a size press cannot satisfy the requirements of inkjet recording, it may be necessary to use specialty paper having a porous coating applied to the recording paper surface. The porous coating comprises pigments, binders, aids, etc. The pigments should be materials with high porosity and low refractive index for high ink absorption and color density. More specifically, amorphous silica, hydrated alumina, soft calcium carbonate, magnesium carbonate, talc, etc., are used, while amorphous silica is used most often. The binder may be a water-soluble binder resin such as polyvinyl alcohol, polyvinylpyrrolidone, etc. By such an ink-absorbing porous coating, feathering along the pulp fibers of the paper is prevented, resulting in enhanced image qualities with improved true roundness of ink droplets.

[0004]

Problems to be solved by the invention

The ink absorption layer in the conventional inkjet recording specialty paper has thus far been described. However, the prior art has the problems described below. To absorb jet inks by the ink absorption layer alone, the ink absorption layer has to be made very thick. However, a thick ink absorption layer may result in reduced mechanical strength of the recording paper. While amorphous silica has high absorption properties, it is difficult to obtain a high solids solution for absorption layer formation. Thus, to obtain a thick coat, the coating has to be formed in many layers, which would greatly increase production cost. In the case of absorption of inks

by both the ink absorption layer and the paper support, it seems possible to reduce the absorption layer thickness. For prevention of ink strike-through, etc., to stop the ink near the support paper surface, it is necessary that the support paper be subjected to a prior sizing by porous pigments such as calcined kaolin, silica, soft calcium carbonate, etc. This would also increase the production cost. Compared with regular paper, in both cases, with the use of large amounts of inorganic pigments, the recording paper becomes very heavy with no rigidity and reduced workability with pencil writing, etc. In some cases, the silanol groups present on the surface of the silica particles may reduce light resistance and storability, due to its photoactive nature. In general, in jet inks, mainly water-soluble dyes containing anionic groups such as sodium sulfonate group, sodium carboxylate group, ammonium carboxylate group, etc., are used. Such water-soluble dyes simply penetrate the absorption layer and dry there, with no chemical bonding with the absorption layer. Thus, the images formed have very poor water resistance. In such circumstances, as a result of an intense study for inkjet recording specialty paper with rapid ink drying and high image durability, we have reached the following invention.

[0005]

Means to solve the problems

Namely, the present invention concerns inkjet recording specialty paper, characterized by having a support covered by an ink absorption layer, wherein the absorption layer contains polyester-based hollow porous resin particles that contain 20-2000 Eq/ton cationic groups as the ionic group.

[0006]

In the present invention, the hollow porous polyester particles comprise mainly a crosslinked resin obtained by the polymerization of 5-99 wt% of vinyl monomer and 1-95 wt% of 20-2000 Eq/ton cationic group-containing polyester resin obtained by condensation of a polycarboxylic acid component preferably containing 5 mol% or more of unsaturated polycarboxylic acid and polyhydroxy alcohol component, and said particles are crosslinked polyester hollow particles with volume-average particle diameter (D) 0.5-100 μm , with one or more independent voids filled with gas or liquid inside the particles, and with a void content of 1-99 vol%. It is preferred that the particles of the present invention have volume-average particle diameter (D) 0.5-100 μm , preferably 1-50 μm , more preferably 2-25 μm , more preferably 2-15 μm , more preferably 2-9 μm . With the volume-average particle diameter below this range, handling becomes difficult, while with the diameter above this range, they are not practical as coating additives, etc. It is desirable that the particle diameter distribution of the particles of the present invention is such that the particle in the diameter range 0.5-2.0 D occupy more than

70 wt% of the total, preferably above 80 wt%, more preferably above 85 wt%, more preferably above 90 wt%. In other words, more than 70 wt% of the particles should be in the range of 0.6-1.8 D, preferably 0.7-1.5 D, more preferably 0.8-1.3 D, more preferably 0.9-1.2 D. The coefficient of variation obtained by dividing the standard deviation by the average value should be below 30%, preferably below 20%, preferably below 15%, more preferably below 10%.

[0007]

The particles of the present invention contain one or more independent voids or voids connected to each other inside the particles. The void content should be 1-99 vol% in the present invention. Here, the void content is the value obtained by dividing the particle interior volume by the particle apparent volume. The void content is preferably 2-98 vol%, preferably 5-95 vol%, more preferably 10-95 vol%, more preferably 20-90 vol%. Such voids are filled with gas or liquid. The gas may be air, nitrogen, carbon dioxide, etc., and the liquid is preferably water. When dry, in the case of voids filled with gas, the particles of the present invention have apparent specific viscosity of but not limited to 0.1-1.3, preferably 0.2-1.2, more preferably 0.5-1.0.

[0008]

The particles of the present invention comprise mainly crosslinked resin obtained by polymerizing 5-99 wt% of vinyl monomer and 1-95 wt% of polyester resin. Here, the polyester resin should be 10-90 wt% of the overall resin component, preferably 20-80 wt%, more preferably 30-70 wt%. The polyester resins in the present invention comprise polycarboxylic acids and polyhydroxy alcohols. The polycarboxylic acids used in polyester resins are, e.g., aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, orthophthalic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 9,10-anthracenedicarboxylic acid, 9,10-anthracenedipropionic acid, diphenic acid;

- aromatic oxycarboxylic acids such as p-hydroxybenzoic acid, p-(hydroxyethoxy)benzoic acid, etc.;
- aliphatic dicarboxylic acids such as succinic acid, adipic acid, azelaic acid, sebacic acid and dodecanedicarboxylic acid, etc.;
- aliphatic unsaturated polycarboxylic acids such as fumaric acid, maleic acid, itaconic acid, mesaconic acid, citraconic acid, etc.;
- aromatic unsaturated polycarboxylic acids such as phenylenediacrylic acid, etc.;
- alicyclic dicarboxylic acids such as hexahydrophthalic acid, tetrahydrophthalic acid, etc.;
- trivalent or higher polycarboxylic acids such as trimellitic acid, trimesic acid, pyromellitic acid, etc.

- In the present invention, monocarboxylic acids may also be used as a portion of the polycarboxylic acids. The monocarboxylic acids may be aromatic monocarboxylic acids, e.g., benzoic acid, chlorobenzoic acid, bromobenzoic acid, p-hydroxybenzoic acid, naphthalenecarboxylic acid, 4-methylbenzoic acid, 3-methylbenzoic acid, salicylic acid, thiosalicylic acid, phenylacetic acid, and lower alkyl esters thereof, cyclohexylaminocarbonylbenzoic acid, n-dodecylaminocarbonylbenzoic acid, t-butylbenzoic acid, naphthalenecarboxylic acid, anthracenecarboxylic acid, t-butyl naphthalenecarboxylic acid, etc., while using t-butylbenzoic acid is preferred. Based on the acid component, the amount of the aromatic monocarboxylic acid used should be 2-25 mol%, preferably 5-20 mol%, more preferably 8-16 mol%.

[0009]

In the present invention, it is essential that the polycarboxylic acid component contain more than 5 mol% of unsaturated aliphatic polycarboxylic acid. In the present invention, the unsaturated polycarboxylic acid may be fumaric acid or maleic acid, while fumaric acid is more preferred. The unsaturated polycarboxylic acid content in the acid component should be above 5 mol%, preferably 20-50 mol%, more preferably 30-50 mol%.

[0010]

The polyhydroxy alcohols used in the polyesters may be aliphatic polyhydroxy alcohols, alicyclic polyhydroxy alcohols, or aromatic polyhydroxy alcohols.

- The aliphatic polyhydroxy alcohols may be aliphatic diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 2,3-butanediol, 1,4-butanediol, the 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol and 2,2,4-trimethyl-1,3-pentanediol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, etc.; triols and tetraols such as trimethylolethane, trimethylolpropane, glycerin, pentaerythritol, etc.
- Alicyclic polyhydroxy alcohols may be 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, spiroglycol, hydrogenated bisphenol A, ethylene oxide adducts and propylene oxide adducts of hydrogenated bisphenol A, tricyclodecanediol, tricyclodecanedimethanol, etc.
- Aromatic polyhydroxy alcohols may be p-xylylene glycol, m-xylylene glycol, o-xylylene glycol, 1,4-phenylene glycol, ethylene oxide adducts of 1,4-phenylene glycol, bisphenol A, ethylene oxide adducts and propylene glycol adducts of bisphenol A, etc.
- Polyester polyols may be lactone polyester polyols obtained by ring-opening polymerization of lactones such as ϵ -caprolactone, etc.
- As with carboxylic acids, monoalcohols such as aliphatic alcohols, aromatic alcohols, alicyclic alcohols, etc., can also be used.

[0011]

In the present invention, the polyesters should have a glass transition temperature above 40°C, preferably above 45°C, more preferably above 50°C, more preferably above 60°C, more preferably above 70°C. With a glass transition temperature below this range, blocking tends to occur during handling or storage, making handling of the powder very difficult in some cases. The polyester resins of the present invention should have number-average molecular weight 1000-20000, preferably 2000-5000, more preferably 3000-4000.

[0012]

In the present invention, it is essential that the polyester resins contain cationic groups in the 20-2000 Eq/ton range. The cationic groups may be primary to tertiary amino groups. The monomers used for introducing cationic groups into the polyester resins may be 2-aminopropane-1,3-diol, 2-dimethylaminopropane-1,3-diol, 2-diethylaminopropane-1,3-diol, dimethylaminoethanol, diethylaminoethanol, diethylaminopropanol, di(hydroxyethyl)amine, di(hydroxybutyl)amine, tri(hydroxyethyl)amine, tri(hydroxybutyl)amine, etc.

[0013]

The vinyl monomers used for crosslinking the polyesters of the present invention may be, e.g., (meth)acrylic acid esters such as C₁₋₁₀-alkyl (meth)acrylate, methoxyethyl (meth)acrylate, hydroxyethyl (meth)acrylate, phenyl (meth)acrylate, cyclohexyl (meth)acrylate, glycidyl (meth)acrylate, etc.; unsaturated ketones such as methyl vinyl ketone, phenyl vinyl ketone, methyl isopropenyl ketone, etc.; vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, etc.; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether, etc.; vinyl halides and vinylidene halides; acrylamide and its alkyl-substituted compounds; styrene, divinylbenzene, alkyl-substituted compounds of styrene, halogen-substituted compounds of styrene, allyl alcohol and its esters or ethers; vinyl aldehydes such as acrolein, metacrolein, etc.; vinyl monomers such as acrylonitrile, methacrylonitrile, vinylidene cyanide, etc.; unsaturated carboxylic acids and their salts such as acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, etc.; unsaturated hydrocarbon sulfonic acids and their salts such as vinylsulfonic acid, acrylic sulfonic acid, p-styrenesulfonic acid, etc.; pyridine, vinylpyrrolidone, vinylimidazole, vinylcarbazole, dimethylaminoethyl (meth)acrylate, diethyl aminoethyl (meth)acrylate, etc. In addition, monomers undergoing ring-opening polymerization, such as siloxanes, lactones, lactams, and epoxy compounds can also be used.

[0014]

Known initiators can be used without any restrictions for reaction initiators, e.g., organic peroxide initiators such as benzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, caprylyl peroxide, lauryl peroxide, acetyl peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, bis(1-hydroxycyclohexyl peroxide), hydroxyheptyl peroxide, t-butyl hydroperoxide, p-menthane peroxide, cumene hydroperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, di-t-butyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(peroxybenzoate), t-butyl perbenzoate, t-butyl peracetate, t-butyl peroctoate, t-butyl peroxyisobutanoate, di-t-butyl-di-perphthalate, persuccinic acid, etc.; and other initiators such as azobisisobutyronitrile, disoxybenzoyl [sic], phenylacetaldehyde, phenylpyroglucose, pinaconic acid derivatives. The reaction accelerators may be cobalt, vanadium, manganese, tertiary amine, quaternary ammonium salt, mercaptan type, etc.

[0015]

Next, specific methods are described for obtaining the hollow crosslinked polyester resin particles of the present invention. The hollow crosslinked polyester resin particles of the present invention can be obtained largely by two methods: (1) hollow polyester particles are formed, impregnated with vinyl monomer by swelling and then subjected to postcrosslinking; (2) the hollow polyester particle formation and crosslinking can be carried out simultaneously.

[0016]

(1) Method for obtaining hollow polyester resin particles

1) Formation of polyester particles with simultaneous hollowing

a) For example, a cationic group-containing polyester resin is dissolved in a water-soluble organic solvent and treated with water to form W/O/W emulsion to obtain hollow particles.

2) Method for making solid polyester particles hollow by posttreatment

a) The cationic group-containing polyester resin solid particles are heated above the glass transition temperature in an aqueous medium.

b) An aqueous dispersion of cationic group-containing polyester resin particles is treated with a water-soluble organic compound, and the water-soluble organic compound is removed as an azeotrope to effect hollowing.

c) An aqueous dispersion of cationic group-containing polyester resin particles is treated with a solvent with swelling of the particles then dried by spray drying, etc., to effect hollowing.

In each method of 2) a)-b). the polyester solid particles may be obtained by classifying the cationic group-containing polyester resin, while using polyester resins obtained by aqueous

granulation described later is preferred. The hollow particles obtained are swelled by vinyl monomer and subjected to postcrosslinking to obtain hollow particles of crosslinked polyesters.

[0017]

(2) Simultaneous formation and crosslinking of hollow polyester particles

1) The solid particles of cationic group-containing polyester resin are swelled by vinyl monomer in an aqueous medium and at the same time heated above the glass transition temperature for simultaneous hollowing and crosslinking.

The solid polyester particles used may be those classified as above, while polyester resins particles obtained by aqueous granulation are preferred.

[0018]

Next, a method for forming polyester particles by aqueous granulation is explained. The cationic group-containing polyester resins of the present invention have dispersibility in water. The aqueous microdispersion of the cationic group-containing polyester resins can be obtained by known methods. Namely, a cationic group-containing polyester resin and water-soluble organic compound are mixed at 50-200°C, then treated with water or water is added to a mixture of a cationic group-containing polyester resin and water-soluble organic compound and then stirred at 40-120°C. Or, a cationic group-containing polyester resin is added to a mixture of water and water-soluble organic compound and stirred at 40-100°C. The water-soluble organic compound may be ethanol, butanol, isopropanol, ethyl cellosolve, butyl cellosolve, dioxane, tetrahydrofuran, acetone, methyl ethyl ketone, etc. Surfactants may also be used without any restrictions. The average particle diameter of such aqueous microdispersion is usually 0.01-1.0 μm . The aqueous microdispersion of the cationic group-containing polyester resin may be treated with electrolytes, etc., under the condition of the cationic group-containing polyester resins being plasticized for gradual particle growth of the microdispersed particles to obtain polyester particles.

[0019]

The electrolytes that can be used in the present invention may be common organic or inorganic water-soluble salts such as sodium sulfate, ammonium sulfate, potassium sulfate, magnesium sulfate, sodium phosphate, sodium dihydrogen sulfate, disodium hydrogen phosphate, ammonium chloride, calcium chloride, cobalt chloride, strontium chloride, cesium chloride, barium chloride, nickel chloride, magnesium chloride, rubidium chloride, sodium chloride, potassium chloride, sodium acetate, ammonium acetate, potassium acetate, sodium benzoate, etc. The electrolyte concentration may be 0.01-2.0 mol/L, preferably 0.1-1.0 mol/L.

more preferably 0.2-0.8 mol/L in the case of monovalent electrolytes, and smaller amounts in the case of polyvalent electrolytes. In the present invention, the electrolytes are added to the system in advance, while the desired effects can be obtained sufficiently also by postaddition. However, good quality polyester resin particles can be obtained by “forming the electrolyte after addition of electrolyte precursor.” The electrolyte precursors may be, e.g., salts that are not very soluble at low temperature but highly soluble at high temperature, compounds undergoing decomposition into electrolytes by pH, temperature, pressure, light, etc. In the present invention, preferred electrolyte precursors are ester compounds from aminoalcohols and carboxylic acids. Such ester compounds are soluble in water, due to the amino group, and aqueous solutions are alkaline. When this aqueous alkaline solution is heated, the ester bonds undergo hydrolysis to give aminoalcohol carboxylate salts. Essentially, the amino group functions as a primary, ammonium secondary or tertiary ammonium group. The preferred amino alcohols in the present invention are aminoethanol, 1,3-aminopropanol, 1,4-aminobutanol, dimethylaminoethanol, 1,3-dimethylaminopropanol, diethylaminoethanol, diethylaminopropanol, etc. The carboxylic acids are, e.g., benzoic acid and its derivatives, naphthalenecarboxylic acid and its derivatives, salicylic acid, thiosalicylic acid, phenylacetic acid, acetic acid, propionic acid, butyric acid, octanoic acid, decanoic acid, dodecanoic acid, lauric acid, stearic acid, acrylic acid, methacrylic acid, etc. In the present invention, esters of any desired combination of aminoalcohols and carboxylic acids can be used as the electrolyte precursors.

[0020]

The polyester particles thus obtained are essentially spherical with a sharp particle size distribution and are dyeable by high-temperature disperse dyeing with high color density. The polyester particles thus obtained can be controlled freely for volume-average particle diameter in a range of 1-100 μm (by electrolyte concentration, temperature, time), and the particle diameter distribution is such that particles in the 0.5-2.0 D range occupy more than 80 wt% of the total with coefficient of variation below 30%. The essentially spherical polyester particles have average sphericity (short diameter/long diameter) above 0.8. Compared with vinyl polymer particles obtained by suspension polymerization, etc., the uniqueness of the particles of the present invention are not only in the diverse polyester resin properties, but also displayed in such polyester particle shapes and particle size distribution. In general, suspension polymerized particles have a broad particle size distribution with coefficient of variation above 30%. However, in the present invention, with control of particle formation conditions, the content of particles in the particle diameter 0.5-2.0 D range is above 80 wt%, preferably above 85 wt%, more preferably above 90 wt%, more preferably above 95 wt% of the total. The coefficient of variation is below 30%, preferably below 20%, more preferably below 15%, more preferably

below 10%. The average sphericity (short diameter/long diameter) is above 0.8, preferably above 0.85, more preferably above 0.9, more preferably above 0.95. The coefficient of variation is the value obtained by dividing the standard deviation by the average value.

[0021]

In the present invention, preferably, hollowing and crosslinking are carried out using the polyester particles thus obtained as seed particles. The polyester particles obtained by aqueous granulation show excellent dispersion stability in aqueous media, no coagulation in swelling by vinyl monomers or heat treatment above the glass transition temperature, and the crosslinked hollow resin particles retain the particle size distribution of the polyester seed particles, with the content of particles in the diameter range of 0.5-2.0 D being above 80 wt% of the total, preferably above 85 wt%, more preferably above 90 wt%, more preferably above 95 wt%, with coefficient of variation below 30%, preferably below 20%, more preferably below 15%, more preferably below 10%, more preferably below 7%. In the present invention, using heat treatment above the glass transition temperature is most preferred. By this method, the void content can be freely controlled by heating temperature and electrolyte concentration in the system. The treatment temperature is preferably from the polyester glass transition temperature to 200°C, preferably below 140°C, more preferably below 100°C, more preferably below 90°C. The electrolyte concentration should be below 0.2 mol/L, preferably below 0.1 mol/L, more preferably below 0.05 mol/L.

[0022]

The polyester resin particles of the present invention can be incorporated with different aqueous dispersions by heterocoagulation during the particle growth process. Polyester microdispersions colored by dyes, etc., can also be obtained. Namely, coloring and making the particles functional can be done. The different type of aqueous dispersions are, e.g., dispersions of pigments, latexes, carbon black, etc. The particles obtained are washed, freed from water and dried by freeze-drying, spray-drying, flow-drying, vacuum-drying, etc. Depending on the cases, of course, the dispersion themselves can be used. The content in the interior voids can be changed.

[0023]

The hollow porous polyester particles thus obtained are made into coating solutions together with binders and other aids, coated on a support and dried to form an absorption layer. Binders may be natural or semisynthetic polymers such as modified starch, carboxymethyl cellulose, hydroxyethylcellulose, methylcellulose, casein, gelatin, natural rubber, etc.; polyvinyl

alcohol, polyvinylpyrrolidone, isoprene, neoprene, polybutadiene, and other polydienes; polyalkenes such as polybutene, polyisobutylene, polypropylene, polyethylene, etc.; vinyl polymers and copolymers such as vinyl halides, vinyl acetate, styrene, (meth)acrylic acid, (meth)acrylic acid esters, (meth)acrylamide, methyl vinyl ether, etc.; polyesters, polyurethanes, polyamides, styrene-butadiene, methyl methacrylate-butadiene-maleic acid synthetic rubber latexes, etc., which are so-called coating binders. In the present invention, using water-soluble binders is preferred.

[0024]

The binder content can be controlled within the range of no adverse effects on the action of the hollow particles. In general, it is below 500 wt%, preferably 0.01-200 wt% of the particles. Various aids can be used, e.g., inorganic and organic pigments such as calcium carbonate, talc, kaolin, titanium oxide, aluminum hydroxide, zinc oxide, urea-formaldehyde resin microparticles, melamine resin microparticles, guanamine resin microparticles; dyes for control of color and whiteness; UV absorbers and antioxidants for improving storability, dispersants, wetting agents, defoamers, etc., for coatability. In the inkjet recording specialty paper of the present invention, when the absorption layer thickness is less than 1 μm , the desired effects cannot be expected. Thus, the absorption layer thickness should be above 3 μm , preferably 5-50 μm . When the average particle diameter of the hollow porous resin particles comprising the absorption layer is smaller than 1 μm , the absorption effect is not realized at all. On the other hand, at above 50 μm , surface properties are poor. Thus, the average particle diameter of the hollow particles should be in the range of 1-20 μm , which is a preferred practical embodiment of the present invention.

[0025]

For improving writability, etc., the absorption layer may further contain, e.g., inorganic or organic pigments such as heavy or light calcium carbonate, talc, clays, natural and synthetic silicates, titanium oxide, aluminum hydroxide, zinc oxide, urea resins, aldehyde resin powder, etc.; various other additives such as UV absorbers, antioxidants, antistatic agents, releases, lubricants, etc. The supports may be regular paper, synthetic paper, synthetic resin film, etc. Here, "regular paper" means the paper based on cellulose pulp, treated with strengthening agents, size, fixer, inorganic or organic filler, etc., and prepared in the usual manner and also includes such paper further treated for size pressing using oxidized starch, etc. or treated with a precoating of pigment such as clay, etc. for improved surface properties, while papers with excellent surface smoothness, such as art paper, coated paper, cast-coated paper, etc., are preferred. Synthetic paper is preferably from polyesters, polypropylene, etc. In the present invention, polyester-based synthetic paper is especially preferred for its excellent adhesion with the binder resins. Before or

after installation of the absorption layer, an anchor coat may be applied to the support for control of adhesion properties, barrier properties, smoothness, hiding properties, etc., or a thin film may be laminated.

[0026]

Action

The inkjet recording specialty paper of the present invention thus obtained has good ink absorption properties with rapid ink drying and no feathering, thus high-quality characters and good images can be formed. The added particles have good adhesion with the binder resins and the support paper, with good mechanical strength, rigidity, good touch and workability such as for pencil writing. In general, for jet inks, water-soluble dyes having anionic groups such as sodium sulfonate group, sodium carboxylate group, ammonium carboxylate group, etc., and dyes classified as acid dyes and direct dyes in the Color Index are mainly used. In the present invention, with the cationic ionic group in the hollow porous particles compounded in the ink absorption layer, the absorbed dyes form ion couples with the cationic group, resulting in high fixation of ink dyes and improved water resistance of the recorded images.

[0027]

Next, examples are illustrated for explanation of the present invention in further detail. However, the present invention is not limited to such examples.

Application example

Polymerization of polyester resin (A1)

In an autoclave fitted with a thermometer and stirrer were placed:

dimethyl terephthalate	47 parts by weight
dimethyl isophthalate	47 parts by weight
ethylene glycol	20 parts by weight
2-aminopropane-1,3-diol	10 parts by weight
bisphenol A-ethylene oxide adduct	240 parts by weight
tetrabutyl titanate	0.1 part by weight

The resulting mixture was heated at 120-220°C for 120 min for ester exchange reaction, then the temperature was reduced to 180°C followed by treatment with:

fumaric acid	58 parts by weight
hydroquinone	0.1 part by weight

The reaction was continued at 200°C for 60 min. The reaction system temperature was raised to 220-240°C. and the reaction was continued under 1-10 mmHg vacuum for 60 min to

obtain a copolymerized polyester resin (A1). NMR analysis of the copolymerized polyester (A1) gave:

terephthalic acid	25 mol%
isophthalic acid	25 mol%
fumaric acid	50 mol%
ethylene glycol	18 mol%
2-aminopropane-1,3-diol	7 mol%
bisphenol A-ethylene oxide adduct	75 mol%

The glass transition temperature was 61°C, acid value 0.08 [mg 50/KOH g], GPC number-average molecular weight was 4500, and amino group equivalent 187 E/kg.

[0028]

Manufacture of polyester aqueous dispersion

A mixture of 300 parts by weight of polyester resin (A1), 150 parts by weight of methyl ethyl ketone and 140 parts by weight of tetrahydrofuran was heated at 80°C for dissolution and treated with 680 parts by weight of water at 80°C to obtain an aqueous microdispersion of the copolymerized polyester resin of particle diameter about 0.1 μm , which was placed in a distillation flask, distilled until the distillate temperature reached 100°C, allowed to cool, treated with water and freed from solvent to obtain a 30%-solids polyester aqueous microdispersion (B1) with 30% solids.

[0029]

Manufacture of polyester particles

In a 1-L 4-neck separatory flask fitted with a thermometer, condenser, and stirrer was heated 300 parts by weight of the polyester aqueous microdispersion (B1) to 80°C, followed by addition of 40 parts by weight of a 20 wt% aqueous solution of dimethylaminoethyl methacrylate over a period of 60 min (0.2 mol/L), stirring at 80°C for 300 min, showing a system conductivity increase from about 1 mS to 25 mS and a pH drop from 10.8 to 6.7, indicating complete hydrolysis of the added dimethylaminoethyl methacrylate to form dimethylaminoethanol methacrylate salt. The copolymer in submicron size in the polyester aqueous microdispersion grew with time to give polyester spherical particles (C1) with average particle diameter (D) 4.2 μm according to a Coulter counter, and more than 94% of particles in the particle diameter range of 0.5-2.0 D.

[0030]

Preparation of hollow particles

The polyester particles (C1) were dewatered, washed, dispersed in water and diluted with deionized water to give a polyester particle dispersion with 5% solids, and 1000 parts by weight of this polyester dispersion were gently stirred in a separatory flask and heated at 90°C for 30 min and cooled by pouring 2000 parts by weight of deionized water into it, and the particles obtained were dewatered and washed on a suction filter and redispersed in water to obtain hollow polyester particles (D1).

[0031]

Crosslinking

The hollow polyester particle (D1) dispersion was diluted with deionized water to 5% solids content, and 1000 parts by weight of this polyester aqueous dispersion were stirred gently in a separatory flask while treated dropwise with 50 parts by weight of 1 wt% benzoyl peroxide solution in styrene, stirred for 30 min, heated to 80°C and allowed to react further for 300 min. The reaction mixture was allowed to cool to room temperature, and particles thus obtained were dewatered and washed on a suction filter and dried in vacuo to obtain hollow crosslinked polyester dry particles (E1) with average particle diameter (D) 5.3 μm , 0.5-2.0 D content above 98%, coefficient of variation 8.7% and void content 54%. The void content was obtained by density difference of particles.

[0032]

Coating

Application Example 1

A mixture of 100 parts (solids) of the interior void-containing hollow crosslinked polyester particles (E₁) thus obtained and 200 parts of polyvinyl alcohol aqueous solution (solids content 34%) was coated as the absorption layer on a commercially available wood-free paper (basis weight 81 g/m², paper press 80 μm) to a dry coating weight of 10 g/m² and dried to obtain inkjet recording specialty paper (F1).

[0033]

Application Example 2

Similar specialty paper (F2) was obtained using the hollow crosslinked polyester particles (E1) coated on polypropylene synthetic paper Upo FPG-80 (product of Oji Yuka Goseishi Co.) as the support in place of the wood-free paper.

[0034]

Application Example 3

Similar specialty paper (F3) was obtained using the hollow crosslinked polyester particles (E1) coated on polyester synthetic paper Kurisupa 1G1111 (product of Toyobo Co.) as the support in place of the wood-free paper.

[0035]

Application Example 4

Similar specialty paper (F4) was obtained using the hollow crosslinked polyester particles (E1) coated on polyester synthetic paper Kurisupa 1G1212 (corona treatment grade) (product of Toyobo Co.) as the support in place of the wood-free paper.

[0036]

Comparative Example 1

Inkjet recording specialty paper (F5) was prepared similarly as in Application Example 1 by replacing the polyester hollow particles by 85 parts by weight of amorphous silica particles and 15 parts by weight of talc powder in the absorption layer coating solution.

[0037]

Comparative Example 2

Inkjet recording specialty paper (F6) was prepared similarly as in Application Example 1 by replacing, in the absorption layer coating solution, the polyester hollow particles with 15 parts by weight of thermally expandable hollow particles (Microsphere F-30, product of Matsumoto Yushi Seiyaku Co.) and 85 parts by weight of titanium oxide powder.

[0038]

Comparative Example 3

Inkjet recording specialty paper (F7) was prepared similarly as in Application Example 1 by replacing, in the absorption layer coating solution, the polyester hollow particles of Application Example 1 with 100 parts by weight of the particles (C1) before hollowing and crosslinking.

[0039]

Evaluation

The 8 different inkjet recording specialty paper samples were subjected to the quality comparison test shown below. Results are given in Table 1. Under a standard environment of

25°C and 60% RH, using an inkjet printer MJ-500 (product of Seiko-Epson Co.) and standard ink, paper samples from the application examples and comparative examples were printed with a 70 mm x 70 mm solid pattern and Chinese characters and measured for recording density of the solid pattern using a Macbeth densitometer (RD-914). The Chinese character print was touched by a finger 10 seconds after printing, and the ink drying speed was evaluated according to the ink residue on the finger. The Chinese character print was observed under a 25X magnifying glass and evaluated visually according to the following standards for dot regeneration and feathering.

Evaluation standard

A: no feathering, good dot roundness.

B: slight feathering, but no practical problems

C: feathering substantial, poor dot roundness

D: lacking dot roundness due to feathering, no practical usability

After drying, the printed portion of the recording paper was immersed in deionized water for 10 sec, lifted out and evaluated for water resistance according to the presence of feathering.

[0040]

Table 1

	①	②	③	④
	記録濃度	乾 燥	画 質	耐水性
⑤ 実施例 1	2. 2	○	A	○
実施例 2	2. 3	○	A	○
実施例 3	2. 3	○	A	○
実施例 4	2. 1	○	A-B	○
比較例 1	2. 0	△	B-C	×
⑥ 比較例 2	1. 9	△-×	B-C	×
比較例 3	1. 6	×	C-D	×

Key: 1 Recording
 2 Drying density
 3 Image quality
 4 Water resistance

- 5 Application Example
- 6 Comparative Example

[0041]

Effect of the invention

As shown clearly by the results in Table 1, the inkjet recording specialty paper obtained in the application examples of the present invention show rapid drying and high-density recording images of good dot roundness and improved water resistance of the recorded images.